



SECTROPHOTOMETRICAL EVALUATION OF THE STABILITY OF MELANINE COMPLEX WITH Cu (II) ION

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Received 20th April 2022,

Accepted 18th May 2022,

Online 28th May 2022

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ABSTRACT: The complex of melanin with Cu (II) ions was synthesized, and the stability constant (β'_K) and molar absorption coefficient (ϵ) of this complex were evaluated by UV-spectroscopic method by the isomolar series method. According to him, the molar absorption coefficient of the complex formed from the cation Cu (II) and melanin at 440 nm is calculated by the isomolar series method $\epsilon_{ij} = 2,26 \cdot 10^{-4}$, and the stability constant is $\beta'_K = 1,02 \cdot 10^{-3}$ was found to be.

KEYWORDS: Melanin, Melanin-Cu(II) complex, UV spectrometer, stability constant, molar absorption coefficient.

INTRODUCTION

It is known that melanin is a group of natural pigments found in most organisms. In organisms, melanin pigments are produced in a special group of cells called melanocytes. Functionally, melanin protects against ultraviolet radiation.

There are five main types of melanin: eumelanin, pheomelanin, neuromelanin, allomelanin, and pyromelanin [1]. The most common type is eumelanin, of which there are two types - brown eumelanin and black eumelanin. Pheomelanin is a derivative of cysteine, which, among other pigments, contains polybenzothiazine components that are largely responsible for the color of red hair. Neuromelanin is found in the brain. Studies have been conducted to study its effectiveness in the treatment of neurodegenerative diseases such as Parkinson's disease. Allomelanin and pyromelanin are two types of nitrogen-free melanin [2]. In human skin, melanogenesis begins under the influence of ultraviolet radiation and leads to darkening of the skin. Melanin is an effective light absorber. It is able to disperse more than 99.9% of the ultraviolet radiation absorbed into the pigment. Due to this property, melanin protects skin cells from damage by ultraviolet radiation [3], reduces the risk of folic acid depletion and skin degradation. Studies have shown

that people with more concentrated melanin, i.e. darker skin, are less likely to develop skin cancer. However, the link between skin pigmentation and photo protection is still unclear [4]. Therefore, the synthesis of internal complex compounds of melanin with various d-metal ions and the assessment of their stability is one of the current problems.

THE PURPOSE OF THE WORK

Synthesis of complex compounds of melanin with copper (II) ions to assess its stability. Also, the study of the evaluation of the stability constant (β'_K) and the molar absorption coefficient (ϵ) of the composition of mixtures in the complex formation by the isomolar series method.

Inspection facilities and measurements

Reagents: Melanin (chemically pure), KBr (Clean for analysis), $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (Clean for analysis), Acetone (Clean for analysis).

Measurements: UV-spectrum spectrophotometer.

Synthesis of Complex

Isomolar series were prepared for UV spectrophotometry in the proportions given in Table 1. Concentrations of reagents obtained for the preparation of isomolar series ranged from 0.0001 mol / l on the basis of which various ratios were formed.

Table 1. Isomolar series

Mixture №	$C \cdot 10^3$, mol/l	
	C_{Me}	C_{R}
1	0,10	0,90
2	0,20	0,80
3	0,30	0,70
4	0,40	0,60
5	0,50	0,50
6	0,60	0,40
7	0,70	0,30
8	0,80	0,20
9	0,90	0,10

THE RESULTS OBTAINED AND THEIR DISCUSSION

The optical densities of the series prepared by the isomolar series method were obtained on a UV spectrometer and used to perform calculations. To study the composition and stability of complex compounds formed in solution under the influence of complexing metals (M) and ligands (R), a series of isomolar solutions with different ratios of initial concentrations of reagents are usually prepared, followed by the optical density (λ) of these solutions at certain wavelengths (l) measured on an ultraviolet (UV) spectrophotometer. The stability constant (β) of complex compounds formed in solution using the isomolar series method is calculated.

Typically, the molar absorption coefficients of these complexes are found along with the stability constants. Classical computational algorithms [5] are not always used, in particular, the stability constants of very strong complexes are incorrectly determined. In our opinion, the accuracy of the assessment of stability constants should depend not only on the strength of the formed complexes, but also on the ratio of the initial concentration of metal (M) and ligand (R) in the model solutions. Incorrectly selected content can lead to large errors or does not allow to calculate the values of the stability constant (β'_K) and the absorption coefficient (ϵ) in general. There are other similar statements in textbooks [6-10].

EXPERIMENTAL PART

Solutions of the reagents were prepared using chemically pure or clean for analysis and precisely weighed portions of reagents for analysis.

This is shown in Table 1, where the optical densities were measured simultaneously at different molar ratios (0.11 to 1.00) with a spectrophotometer with a quartz cuvette thickness $l = 1$ cm.

Table 1. Isomolar series

Mixture №	$C \cdot 10^3$, mol/l		C_{Cu}/C_R	A 440 nm
	C_{Cu}	C_R		
1	0,10	0,90	0,11	0,221
2	0,20	0,80	0,25	0,242
3	0,30	0,70	0,43	0,186
4	0,40	0,60	0,67	0,129
5	0,50	0,50	1,00	0,164
6	0,60	0,40	1,50	0,152
7	0,70	0,30	2,33	0,185
8	0,80	0,20	4,00	0,262
9	0,90	0,10	9,00	0,262

Algorithm for calculating the molar coefficient and stability constant. Suppose that the conditional stability constant of the CuR complex is unknown and it is calculated in the traditional way, as shown in the manual [5]: first two series of the isomolar are selected, and then the molar coefficient is calculated. The molar coefficient of the complex is calculated according to the following formula (1):

$$\varepsilon_{ij} = \sqrt{\frac{A_i \cdot (A_j)^2 - A_j \cdot (A_i)^2}{A_j \cdot C_{Mi} \cdot C_{Ri} - A_i \cdot C_{Mj} \cdot C_{Rj}}}, \quad (1)$$

Where ε_{ij} is the molar absorption coefficient of the complex; C_{Mi} , C_{Mj} , C_{Ri} , C_{Rj} are the initial concentrations of metal (M) ions and ligands (R) in solutions i and j, respectively; A_i and A_j are different optical densities of the same solution at 440 nm. Similar calculations are then performed for other pairs of solutions. The ε_{ij} values obtained for different pairs of solutions differ slightly due to random errors in solution preparation and photometry. Based on the average value of the molar absorption coefficient, the conditional stability constant of the complex under study (β'_K) calculated formula (2):

$$\beta'_K = \frac{A/\varepsilon_K}{\left(C_R - \frac{A}{\varepsilon_K}\right) \cdot \left(C_M - \frac{A}{\varepsilon_K}\right)}, \quad (2)$$

then, according to the algorithm, the stability constant of the same complex is found. The average calculated ε_{ij} value corresponds to the literature data. Thus, the choice of isomolar series used to evaluate the stability of complex compounds by the isomolar sequence method affects the accuracy of this assessment. To obtain sufficiently accurate results, the data obtained for solutions belonging to the same series should be used together (both mixtures should have an excess of metal or reagent).

Thus, at 440 nm, the molar absorption coefficient of the complex was found to be $\varepsilon_{ij} = 2,26 \cdot 10^{-4}$, and the stability constant $\beta'_K = 1,02 \cdot 10^{-3}$.

CONCLUSIONS

1. The complex of melanin with Cu (II) ions was synthesized, and the stability constant (β'_K) and molar absorption coefficient (ε) of this complex were evaluated by UV-spectroscopic method by the isomolar series method.

2. The molar absorption coefficient of the complex formed by the cation of melanin with Cu (II) at 440 nm was found to be $\varepsilon_{ij} = 2,26 \cdot 10^{-4}$ when calculated by the isomolar series method, and the stability constant was $\beta'_K = 1,02 \cdot 10^{-3}$.

REFERENCES:

- [1]. Ogarkov B. N., Ogarkova G. R., Samusenok L. V. Mushrooms - defenders, healers and destroyers. - Irkutsk, 2008.
- [2]. Alekseeva T. N., Oreshchenko A. V., Kulakova A. V., Durnev A. D., Samusenok L. V., Ogarkov B. N. Antimutagenic properties of plant melanin pigment // Storage and processing of agricultural raw materials. - 2001. - № 5. - P. 37—38.
- [3]. Zherebin Yu. M., Sava V. M., Kolesnik A. A., Bogatsky A. V. Studies of the antioxidant properties of enomelanin // Doklady AN SSSR. - 1982. - V. 262, №. 1. - P. 112-115.
- [4]. Zherebin Yu. M., Bondarenko N. A., Makan S. Yu., Finniki V. P., Klemanova N. N., Malikova L. A., Bogatsky A. V., Valdman A. V. Pharmacological properties of enomelanin pigments. // Reports of the Academy of Sciences of the Ukrainian SSR. - 1984. - №. 3. - P. 64-67.
- [5]. Vlasova I.V., Zheleznova T.Yu., Vershinin V.I. Choice of model solutions for spectrophotometric assessment of the stability of complex compounds using the method of isomolar series // Vestnik. Omsk University. - 2012.- №2. - P. 127-130.
- [6]. Stolpovskaya E. V., Trofimova N. N., Babkin V. A., Khutsishvili S. S., Zhitov R. G., Chuparina E. V., Maltsev A. S. Research and optimization of the complex formation reaction of manganese ions (II) with dihydroquercetin in the aquatic environment // Chemistry of vegetable raw materials. – 2020. – №. 3. - P. 47-56.
- [7]. Stolpovskaya E. V., Trofimova N. N., Babkin V. A., Zhitov R. G. Research and optimization of the reaction of complex formation of cobalt ions with dihydroquercetin in an aqueous medium // Chemistry of plant raw materials. – 2019. – №. 1. - P. 95-104.
- [8]. Trofimova N. N., Babkin V. A., Vakulskaya T., Chuparina E. V. Study of methods of synthesis, structure and properties of complexes of flavonoids with metal ions. Message 1. Synthesis and determination of the structure of complexes and salts of dihydroquercetin with zinc, copper (II) and calcium in aqueous solutions // Chemistry of vegetable raw materials. – 2012. – №. 2. - P. 51-62.
- [9]. Trofimova N. N., Stolpovskaya E. V., Babkin V. A. Study of methods of synthesis, structure and properties of complexes of flavonoids with metal ions. Message 2. Optimization of the reaction of complex formation of zinc with dihydroquercetin in the aquatic environment // Chemistry of vegetable raw materials. – 2013. – №. 3. – P. 91-97.
- [10]. Ismatov D.M., Mukhamadiyev N.Q. Spectrophotometric evaluation of the stability of quercetin complex with Fe (II) ion // Innovative technologies for the processing of mineral and technogenic raw materials of the chemical, metallurgical, petrochemical industries and the production of building materials. – 2022. – P. 79-81.